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ELECTROCHEMISTRY OF FUEL CELL ELECTRODES

Computer Programs for Calculations Relating to Dropping Amalgam Electrodes

by

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INTRODUCTION

In the last five years, the increased availability of high-speed electronic computers has greatly enlarged the scope of data-reduction techniques. The calculations of double-layer capacity and overpotential from data taken using a dropping electrode in conjunction with an oscilloscope are not difficult, but are extremely tedious to carry out with an ordinary desk calculator. As a result, many workers have not obtained all the available information from their data and have relied on averaged values which often vary considerably from the true values.

This report describes the computer programs which we have developed for carrying out calculations of double-layer capacity and overvoltage from data taken using a dropping amalgam electrode.

The most conveniently available computers were the IBM 7094-1401 combination, which was used for long calculations (Program 3), and the IBM 1620, which was used for short calculations (Programs 4 and 5). The programs were prepared in the FORTRAN programming language, since both of these computers use FORTRAN compilers as standard procedure.

PROGRAM 3: CAPACITY OF A DROPPING ELECTRODE *

The major program discussed here is one written for the IBM 7094, which accepts raw capacity data and calculates the double-layer capacity, as well as all the thermodynamic parameters which can be obtained from a single capacity-potential curve. Alternative paths are provided so that the capacity can be calculated without performing the integrations, or so that the integrations can be performed on capacity-potential data collected from other sources. A logical diagram of the program is shown in Fig. 1.

The experimental technique and theory on which the calculations are based were developed primarily by Grahame [1, 2], but have been used by many other workers.

The first step in all the calculations relating to dropping electrode is to obtain the area of the drop at the moment when the measurement was taken. A convenient form for the dependence of area on time, which includes a correction for the back-pressure due to interfacial tension, was proposed by Grahame [3]. The pressure P at the capillary tip results from both the height of the amalgam above the tip and the back-pressure due to interfacial tension:

$$P = \rho gh - 2(\gamma / r) \qquad (1)$$

where g is the acceleration of gravity (980.6 dynes/g), h is the height of the column of amalgam, ρ is the density of the amalgam, γ is its interfacial tension, and r is the radius of the drop at the end of the capillary.

The volume flow rate is taken to be proportional to P, and the area of the drop is obtained by integrating the volume flow rate with respect to time, assuming a spherical shape for the drop.

The assumption of a spherical drop is not as drastic as it might appear, since as long as the drop retains its cylindrical symmetry, the area/volume ratio is independent of its size. The error resulting from

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* Programs 1 and 2 were related to a different problem. See Tech. Memo. #11: "Hydrogen Evolution at Solid Indium Electrodes."

the normal asphericity of the drop just before it falls can be avoided by discarding values obtained very close to the end of drop lifetime. The principal uncertainty in area occurs when the drop is initially formed and is not yet a complete sphere. This problem can be minimized experimentally by using fine-pointed capillaries instead of the conventional blunt polarographic capillaries [3].

Making the assumption of a spherical drop, we obtain the following relation for the area of the drop as a function of time:

$$A = (36\pi)^{1/3} (k \rho ght)^{2/3} \left\{ 1 - \frac{3\gamma}{\rho gh} \left(\frac{4\pi\rho}{3mt} \right)^{1/3} \right\}^{2/3} \qquad (2)$$

where k is a proportionality constant, and m is the mass flow of amalgam through the capillary, which is independent of potential [4]. The proportionality constant can be evaluated if one knows the drop lifetime t^*, since the total volume of a drop is simply $m t^* / \rho$. Evaluating (2) at the lifetime of the drop, and calculating the total volume of the drop, we obtain the following expression for the proportionality constant

$$k_1 = \frac{m}{\rho^2 g h} \left\{ 1 - \frac{3\gamma}{\rho g h} \left(\frac{4\pi\rho}{3 m t^*} \right)^{1/3} \right\}^{-1} \qquad (3)$$

This expression may be substituted in (2) to give an equation for the area of a drop as a function of time. Note that when h is very large, (2) and (3) together reduce to the usual formula:

$$A = (36\pi)^{1/3} (m t / \rho)^{2/3} \qquad (4)$$

The true area is smaller than the area calculated from equation (4) because of the back-pressure.

Since it is sometimes difficult to obtain accurately reproducible drop lifetimes, some sort of averaging procedure for drop lifetime is desirable. The drop lifetime used in equation (3) is calculated from the

interfacial tension γ and an average value for the diameter a of the capillary obtained from a number of measurements. The drop lifetime is related to the interfacial tension and capillary diameter by the usual formula for the drop-weight measurement of interfacial tension:

$$t^* = (\pi \gamma a / m g) \qquad (5)$$

Although more subtle corrections [4] are known for this equation, they are not conveniently expressed in analytic form, and were not necessary for the present calculations.

From a number of measurements of drop lifetime, an average value is obtained for the capillary diameter. This can be checked against actual measurements of the capillary diameter with a traveling microscope. From this value, using equation (5), t^* is calculated for each point, and used in (3) to obtain the proportionality constant.

The advantage of this averaging method is that only a few drop lifetimes need be actually measured. The capacity bridge can be balanced at the same point in the oscilloscope trace, whether or not the end of the drop actually appears on the oscilloscope screen [1].

In the above equations a value must be assumed for the interfacial tension in the initial phase of the calculation, but once the capacity data has been integrated, a much better value for the interfacial tension is known. To provide the most rapid convergence, the best possible starting values for interfacial tension are required. These are obtained in the present calculation by intergrating an assumed quadratic form for the integral capacity, which may be obtained from literature data, or guessed by analogy with similar systems. The exact values used affect only the rapidity of convergence, not the final answer.

The integral capacity is assumed to be given by the quadratic form

$$K = K_o + K_1 \varphi + K_2 \varphi^2 \qquad (6)$$

where φ is the rational potential (potential with respect to the point of zero charge). The interfacial tension is then given by

$$\gamma = \gamma_{max} - 10 \left\{ \frac{K_o}{2} \varphi^2 + \frac{K_1}{3} \varphi^3 + \frac{K_2}{4} \varphi^4 \right\} \quad (7)$$

where γ_{max} is the maximum value of the interfacial tension, which must be measured, obtained from the literature, or estimated by correlation with similar systems. For mercury in dilute aqueous solutions, $\gamma_{max} = 426.2$ erg cm^{-2}, $K_c = 27.0$ $\mu f\ cm^{-2}$, $K_1 = 18.65$ $\mu f\ cm^{-2}$ $volt^{-1}$, and $K_2 = 9.65$ $\mu f\ cm^{-2}$ $volt^{-2}$. The factor 10 is required in equation (7) because of the conventional units: one $\mu f\ cm^{-2}$ $volt^2$ is equal to 0.1 erg cm^{-2}.

Further details regarding the relation of drop area to drop lifetime may be found in the literature [5-7].

Once the area of the drop at the point of balance has been calculated, the values of capacity and series resistance read from the bridge can be converted to the desired quantities: capacity per unit area and polarization resistance. The capacity per unit area is simply

$$C = C_{exp} / A \ . \quad (8)$$

The polarization resistance is obtained after correcting the total measured resistance for the resistance of the electrolyte and the resistance of the amalgam in the capillary. If a cylindrical or spherical counter electrode of radius δ surrounds the drop, then the resistance R of the solution is given by

$$R = \frac{\delta r}{K A (r + \delta)} \quad (9)$$

where K is the specific conductance of the electrolyte, r is the radius

and A is the area of the drop at the balance point. The polarization resistance is given by

$$R_{pol} = A (R_{exp} - R - R_{cap}) \qquad (10)$$

where R_{exp} is the resistance measured on the bridge, R is given by equation (9), and R_{cap} is the resistance of the thread of amalgam in the capillary. R_{cap} may be calculated from the dimensions of the capillary and the resistivity of the amalgam. It is rarely more than one or two ohms.

The next portion of the calculation involves integration of the measured differential capacity values to obtain the surface charge, integral capacity, and interfacial tension.

Measurements of capacity are usually taken at quite closely-spaced intervals of potential (0.01 to 0.05 volts). Since the values may scatter slightly about a smooth curve, a simple trapezoidal rule was used for the integration instead of a more sophisticated numerical integration algorithm. The surface charge is obtained by integrating the differential capacity:

$$q = \int_{c}^{\varphi} C \, d\varphi \qquad (11)$$

where φ is the rational potential. A second integration gives the interfacial tension:

$$\gamma = \gamma_{max} - 10 \int_{o}^{\varphi} q \, d\varphi \qquad (12)$$

The absolute value of γ depends, of course, on the value of γ_{max}, which must be obtained independently. The integral capacity is obtained from the surface charge:

$$K = q/\varphi \qquad (13)$$

Once these values have been calculated, the interfacial tension is used in the first part of the program to recalculate the area of the drop, and better values of the differential capacity, surface charge, integral capacity, and interfacial tension are obtained. The iteration is continued until successive values of interfacial tension agree within 0.01 erg/cm^2. The final values do not depend on the initial assumption for the capacity function (eq. 6); this affects only the rapidity of convergence.

The next step in the calculation is to find the potential of the outer Helmholtz plane and to calculate the contribution to the capacities from the diffuse double layer. The potential of the outer Helmholtz plane, Ψ, is given by the equation

$$K^o (\varphi - \Psi) = \sqrt{\frac{2 D D_o RT C}{\pi}} \sinh \frac{F \Psi}{2 RT} \qquad (14)$$

where K^o is the integral capacity of the Helmholtz double layer, D is the dielectric constant of the solvent, D_o (1.1128×10^{-12} coul volt^{-1}cm^{-1}) is a dimensional constant, R is the gas constant, C is the concentration of a 1-1 electrolyte, T is the absolute temperature, and F is the Faraday constant. Analogous equations have been derived for electrolytes other than simple univalent ones, [8], and treatments have been extended beyond the simple Debye-Huckel theory [9-14].

With the constants evaluated and combined, eq. (14) becomes

$$K^o (\varphi - \Psi) = 11.72 \sqrt{C \frac{T}{298}} \sinh \left\{ 19.46 \Psi \left(\frac{298}{T} \right) \right\} \qquad (15)$$

This equation is most easily solved by iteration using Newton's approximation method.

Initially, since we do not know K^o, we approximate K^o by K, the total integral capacity, and calculate a provisional value for Ψ, using equation (15). Then, using this approximate value for Ψ, the

integral capacity of the diffuse double layer, K^d , is calculated:

$$K^d = \frac{11.72}{\psi} \sqrt{C \frac{T}{298}} \sinh \left\{ 19.46 \, \psi \left(\frac{298}{T}\right) \right\} \qquad (16)$$

The integral capacity of the Helmholtz layer is obtained from the total integral capacity and the capacity of the diffuse double layer:

$$\frac{1}{K^o} = \frac{1}{K} - \frac{1}{K^d} \qquad (17)$$

The improved value of K_o is then used in (15) to obtain a better approximation to ψ . The iteration is continued until two successive values of K^d agree to within 0.01 $\mu f/cm^2$.

The differential capacity of the diffuse double layer is calculated from the equation:

$$C^d = 228.5 \left(\frac{298}{T}\right) \sqrt{C \frac{T}{298}} \cosh \left\{ 19.46 \left(\frac{298}{T}\right) \psi \right\} \qquad (18)$$

and the differential capacity of the Helmholtz double layer obtained from this:

$$\frac{1}{C^o} = \frac{1}{C} - \frac{1}{C^d} \qquad (19)$$

This iteration often converges after less than five cycles. The convergence is most rapid for concentrated solutions, since then K^d is very close to K .

In Appendix I is given a complete listing of Program 3, together with the required forms for the input data, and sample input and output data.

PROGRAM 4: OVERVOLTAGE MEASUREMENTS AT A DROPPING ELECTRODE

Conventionally, when current-voltage curves are measured using a dropping electrode, and a simple potentiometer polarizing circuit, either the time-average current or the current at the end of a drop lifetime is used to calculate the current density. Such a method is adequate if the currents are very small, or if only approximate current-potential curves are required. However, under conditions where currents of the order of 1 milliampere are to be drawn, or where more accurate measurements of overvoltage are required, a better method is to observe the instantaneous value of the dropping electrode potential, while applying a constant current to the cell through an external polarizing circuit. The difference between the drop potential and a known bias potential can be displayed on an oscilloscope, and under favorable conditions, the instantaneous potential of the drop can be measured to within 1 or 2 mv. A typical trace is shown in Fig. 2. The constant current can be read from an accurate microammeter, and the current density calculated once the drop area is known.

The calculation of drop area is essentially the same as we have described for the capacity measurements; however, for overvoltage measurements the accuracy required is not so great. An error of 1 mv in measuring hydrogen overvoltage is equivalent to an error of 2% in current density. This means that the back-pressure correction, which is significant for capacity measurements, is unimportant for overvoltage measurements and can be dispensed with. Thus the simpler equation (4) can be used for calculating the area.

$$A = (36\pi)^{1/3} (m t / \rho)^{2/3} \qquad (4)$$

To ease the tedium of measuring several potential-time points on each of several hundred oscilloscope photographs to within 0.01 inches, a Gerber Analog-to-Digital converter, or graph reader, was used. This

device reads the x and y coordinates of a manually-set cross-hair, and enters the information on a punched card in a pre-determined format. Because the coordinates are given on an internal integral scale, 200 units per inch, it was necessary to include provision for horizontal and vertical calibrations in the program.

A complete listing of Program 4, together with the forms for the input data, and sample input and output data, are given in Appendix II.

PROGRAM 5: LEAST-SQUARES ANALYSIS OF CURRENT-POTENTIAL CURVES

The punched card output from Program 4 was used in another program which fitted current-density i and overpotential η measurements to a theoretical curve derived by Frumkin [17, 18] on the assumption that discharge of an ion is the slow step in the electrode reaction mechanism.

$$\eta = \frac{1-\alpha}{\alpha}\psi + \frac{RT}{\alpha F} \ln (i / i_o') \qquad (20)$$

where ψ is the potential of the outer Helmholtz plane, calculated according to equation (14). The integral capacity is assumed to be given by a quadratic expression (eq. 6). Eq. 20 can be cast into the form of a straight line

$$y = \alpha x + B \qquad (21)$$

where

$$x = \eta + \psi \qquad (22)$$

$$y = \psi + \frac{RT}{F} \ln i \qquad (23)$$

$$B = \frac{RT}{F} \ln i_o' \qquad (24)$$

The values of x and y are calculated, and a least-squares fit made to a straight line. The best values of the parameters α and $-\log i_o'$ are calculated, together with their 95% confidence limits.

To fit the current density-potential data to an ordinary Tafel equation

$$\eta = \frac{RT}{\alpha F} \ln (i/i_o) \qquad (25)$$

it is necessary only that ψ should be zero; this is accomplished by setting all the coefficients of the quadratic expression for capacity (eq. 6) equal to zero.

A complete listing of Program 5, together with the requisite forms for the input data, and sample input and output data, is given in Appendix III.

CONVERSION OF 1620 PROGRAMS FOR 7090

Conversion of a program written for the IBM 1620 for use on the IBM 7090 or 7094 involves only the modification of the input-output statements. To convert Programs 4 and 5 for use on the 7090, change every "READ" statement to "READ INPUT TAPE 5" , and every "PUNCH" statement to "WRITE OUTPUT TAPE 6". The only exception is statement 53 of Program 4, which must produce punched card output, and which should read "WRITE OUTPUT TAPE 9".

Under some monitor systems, all of these changes may not be necessary.

CONVERSION OF 7090 PROGRAMS FOR 1620

Conversion of a 7090 program for use on the 1620 is often more difficult than the reverse, and indeed may be impossible because of the more limited storage facilities of the smaller computer. The 7090 program described here (Program 3) requires no more than 4000 words of memory, and so can be adapted to the 1620 with only slight modifications. These modifications are as follows:

1. Change all statements "READ INPUT TAPE 5" to "READ".
2. Change all statements "WRITE OUTPUT TAPE 6" to "PUNCH".
3. Change all statements "WRITE OUTPUT TAPE 9" to "PUNCH". (the punched output for re-entry to the program will have to be separated from that which is to be printed.)
4. Instead of the REREAD subroutine, the title card must be read as a dimensioned variable. Delete the REREAD statement at the beginning of the program. Include in the dimension statements, a variable TITLE (20).

Statements 1 and 2 should read:

```
1 READ    2, KK, TITLE
2 FORMAT (I1, I3, 19I4)
```

Statements 350 and 351 should be deleted.

5. The functions defined in statements 123, 38, 39, 179, and 180 at the beginning of the program must be included explicitly in the statements which refer to them: statements 28, 50, 152, 184, 185, 191, 197, 198, 205, 211.

Unless only a very small amount of data is to be processed, or a faster computer is not available, it is not recommended that Program 3 be used on the 1620, since the time for compiling and executing it will be inordinately long.

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APPENDIX I

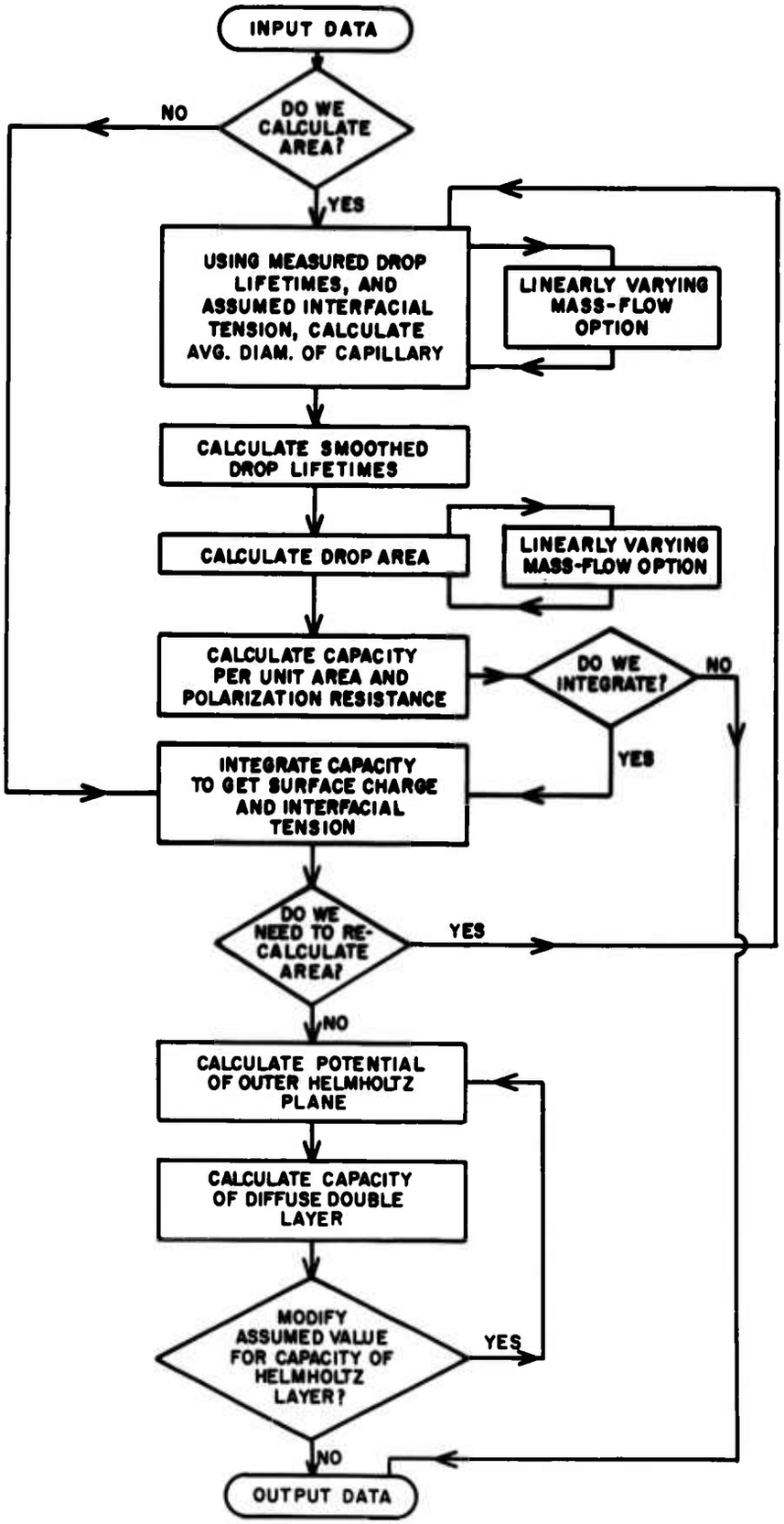
Figure 1 - Logical diagram for Program 3

Listing of Program 3

Text describing input data for Program 3

Sample data

LOGICAL DIAGRAM FOR PROGRAM 3 (CAPACITY)



```
 1     CAPACITY OF A DROPPING AMALGAM ELECTRODE - PROGRAM 3-                    5/09/64

C2     INPUT OFF-LINE ON A2 - LOGICAL 5                                  3      2
C3     PRINTED OUTPUT OFF-LINE ON A3 - LOGICAL 6                         3      3
C4     PUNCHED OUTPUT OFF-LINE ON A5 - LOGICAL 9                         3      4
C
F      REREAD                                                            3     4A
       DIMENSION NUM1(80), NUM2(80), CAPG (80), ATENS (80)               3      5
       DIMENSION ETA1(80), T1(80), ETA(80), TIME(80), CAPX(80), RESX (80) 3      6
       DIMENSION  AREA(80), CAP(80), RES(80), PHI(80), CHG(80),CAPINT(80) 3      7
       DIMENSION    CAPH(80), CAPIG(80), CAPIH(80), TENS(80), PSI(80)     3      8
   123 GAMMAF (P) = P*P*(CAP0/2. + CAP1*P/3. + CAP2*P*P/4.) * 10.         3     8A
    38 8RAF(T,G)   = (1.-(Q*G)/(T**(1./3.)))**(2./3.)                     3     8B
    39 TSTARF(G)   = (DIAM*G)/(AM*0.31214)                                3     8C
   179 SINHF(Z) = 0.5(EXPF(Z)-EXPF(-Z))                                   3     8D
   180 COSHF(Z) = 0.5(EXPF(Z)+EXPF(-Z))                                   3     8E
C
     1 READ INPUT TAPE 5, 350, KK                                         3      9
   350 FORMAT (I1)                                                        3     9A
   351 READ INPUT TAPE 99, 2                                              3     9B
     2 FORMAT (72H----------------THIS SPACE IS FOR A TITLE------------- 3     10
    1----------------)                                                    3     11
   313 IF (KK - 1)  314, 316, 420                                         3    11A
   420 IF (KK - 2)  314, 316, 314                                         3     12
   314 WRITE OUTPUT TAPE  6, 2                                            3    12A
   315 GO TO 1                                                            3    12B
   316 WRITE OUTPUT TAPE 6, 2                                             3    12C
C
   124 READ INPUT TAPE 5,5,RHO, HGT, AM, DELTA, TEMP                      3     13
     5 FORMAT(4F8.3,F8.2)                                                 3     14
   255 AMT = AM                                                           3    14A
   230 IF (AMT - 999.99) 6, 231, 232                                      3    14B
   232 WRITE OUTPUT TAPE 6, 233, AMT                                      3    14C
   233 FORMAT (/51H THE TEST NUMBER FOR MASS FLOW RATE IS WRONG. AMT =     3    14D
     1 F8.3)                                                              3    14D
   324 GO TO 1                                                            3    14E
   231 READ INPUT TAPE 5, 234, AM1, AM2                                   3    14F
   234 FORMAT (2F8.3)                                                     3    14G
C
     6 READ INPUT TAPE 5,7, GMAX, ETAZ, CONC,SKAPPA, CRES                 3     15
     7 FORMAT (F8.2, F8.3, 2F8.5, F8.3)                                   3     16
   300 IF (RHO - 99.999) 8, 19, 301                                       3     17
   301 WRITE OUTPUT TAPE 6, 302, RHO                                      3    17A
   302 FORMAT (/51H THE TEST-VALUE FOR RHO IS WRONG. IT IS NOT 99.999- /  3    17B
    115H INSTEAD, IT IS F10.5)                                            3    17C
   320 GO TO 1                                                            3    17D
C
    19 N =0                                                               3     18
    20 N = N+1                                                            3     19
   121 READ INPUT TAPE 5, 21, ETA(N), CAP(N), NUM1(N), NUM2(N)            3     20
    21 FORMAT (F8.3, 8X, F8.2, 8X, 2I4)                                   3     21
   122 IF (ETA(N) - 3.333) 20, 26, 23                                     3     22
    23 IF (ETA(N) - 6.666) 24, 26, 24                                     3     23
    24 WRITE OUTPUT TAPE 6, 17, ETA(N), CAP(N)                            3     24
   321 GO TO 1                                                            3    24A
C
    26 N = N-1                                                            3     25
```

```
1     CAPACITY OF A DROPPING AMALGAM ELECTRODE - PROGRAM 3-                    5/09/64

  126 WRITE OUTPUT TAPE 6, 27, TEMP, CONC, ETAZ, GMAX                    3     26
   27 FORMAT (//8H TEMP = F8.2/ 8H CONC = F8.5/ 8H ETAZ = F8.3/ 8H GMAX  3     27
     1= F8.2)                                                            3     28
  127 GO TO 70                                                           3     29
C
    8 READ INPUT TAPE 5,4, CAPO, CAP1, CAP2                              3     31
    4 FORMAT (3F8.3)                                                     3     30
    9 WRITE OUTPUT TAPE 6, 10, RHO, GMAX, CAPO, HGT, ETAZ, CAP1, AM,     3     32
     1CONC, CAP2, DELTA,SKAPPA, TEMP, CRES                               3     33
   10 FORMAT(//8H RHO  = F8.3,6X,8H GMAX = F8.2,6X,8H CAPO = F8.3/8H HGT 3     34
     1  = F8.3,6X,8H ETAZ = F8.3,6X,8H CAP1 = F8.3/8H FLOW = F8.3,6X,8H  3     35
     2CONC = F8.5,6X,8H CAP2 = F8.3/8H DELTA= F8.3,6X,10H KAPPA =  F8.6,  3     36
     34X, 8H TEMP = F8.2 / 8H CRES = F8.3)                               3     37
C
  250 IF (AMT - 999.99) 11, 251, 256                                     3    37A
  256 WRITE OUTPUT TAPE 6, 233, AMT                                      3    37B
  257 GO TO 1                                                            3    37C
  251 WRITE OUTPUT TAPE 6, 252, AM1, AM2                                 3    37D
  252 FORMAT (/58H THE MASS FLOW RATE USED IS A LINEAR INTERPOLATION BET 3    37E
     1WEEN / 7H AM1 = F8.3, 11H AND AM2 = F8.3)                          3    37F
C
C46   WE NOW EVALUATE THE CAPILLARY DIAMETER                             3     38
   11 M = 0                                                              3     39
   12 M = M + 1                                                          3     40
   13 READ INPUT TAPE 5, 14, ETA1(M), T1(M)                              3     41
   14 FORMAT (F8.3, F8.5)                                                3     42
   15 IF (ETA1(M) - 3.333) 12, 18,16                                     3     43
   16 WRITE OUTPUT TAPE 6, 17, ETA1(M), T1(M)                            3     44
   17 FORMAT (/58H THERE IS NO PROPER END-OF-DATA CARD - THE LAST CARD R  3     45
     1EAD F8.3,2X,F10.5)                                                 3     46
  118 GO TO 1                                                            3     47
   18 M = M - 1                                                          3     48
  119 WRITE OUTPUT TAPE 6, 22                                            3     49
   22 FORMAT (//20H DROP LIFETIME DATA /32H   POT    TIME   GAMMA     DI 3     50
     1A  /)                                                              3     51
   32 FM = M                                                             3    53A
  139 NM = 1                                                             3    53B
  125 SDIA = 0                                                           3    53C
   25 DO 31  I = 1,M                                                     3     54
  303 IF (NM - 1) 28, 28, 330                                            3    54A
  330 DO  332 II = 1, N                                                  3    54B
  331 IF (ETA(II) - ETA1(I))  332, 333, 333                              3    54C
  332 CONTINUE                                                           3    54D
  333 GAM = TENS(II)                                                     3    54E
  305 GO TO 236                                                          3    54F
   28 GAM = GMAX - GAMMAF(ETA1(I)- ETAZ)                                 3    54G
  400 ATENS(I) = GAM                                                     3     55
  236 IF (AMT - 999.99) 129, 237, 238                                    3    55A
  238 WRITE OUTPUT TAPE 6, 233, AMT                                      3    55B
  239 GO TO 1                                                            3    55C
C
  237 FI = I                                                             3    55D
  240 AM = AM1 + (AM2 - AM1) * FI/FM                                     3    55E
  129 DIA = 0.31214* AM * T1(I)/GAM                                      3     56
  130 SDIA = SDIA + DIA                                                  3     57
  306 IF (NM - 1) 29, 29, 31                                             3    57A
```

```
 1    CAPACITY OF A DROPPING AMALGAM ELECTRODE - PROGRAM 3-                    5/09/64

   29 WRITE OUTPUT TAPE 6, 30, ETA1(I), T1(I), GAM, DIA                  3     58
   30 FORMAT (F8.3, F8.5, F8.2, F8.5)                                    3     59
   31 CONTINUE                                                           3     60
   33 DIAM = SDIA/FM                                                     3     62
  307 IF(NM - 1) 34, 34, 242                                             3     62A
   34 WRITE OUTPUT TAPE 6, 35, DIAM, M                                   3     63
   35 FORMAT (/33H AVERAGE DIAMETER OF CAPILLARY = F8.5,12H MILLIMETERS/  3     64
     126H NUMBER OF MEASUREMENTS =  I2)                                  3     65
C
C48   THE NEXT THING TO DO IS CALCULATE THE AREA AND THE CAPACITY         3     67
  242 IF (AMT - 999.99) 36, 309, 244                                     3     67A
  244 WRITE OUTPUT TAPE 6, 233, AMT                                      3     67B
  136 GO TO 1                                                            3     67C
   36 COA = 4.835974*((AM*.001/RHO)**(2./3.))                            3     68
   37 Q = 0.00493164/(HGT*(AM*.001*RHO*RHO)**(1./3.))                    3     69
  309 IF (NM - 1) 57, 57, 150                                            3     72A
   57 WRITE OUTPUT TAPE 6, 2                                             3     72B
  401 WRITE OUTPUT TAPE 6, 58                                            3     73
   58 FORMAT(//57H FIRST APPROXIMATION BASED ON ASSUMED INTERFACIAL TENS 3     74
     1ION     //66H   RUN     POT       TIME   EXP-CAP EXP-RES  AREA    C 3     75
     2AP   POL-RES /66H   NO.    VOLTS      SEC   M-FARADS   OHMS  SQ MM  3     76
     3 MF/SQCM  OHM-CM2/)                                                3     77
C
   40 N = 0                                                              3     78
   41 N = N + 1                                                          3     79
   42 READ INPUT TAPE 5, 43, ETA(N), TIME(N), CAPX(N), RESX(N), NUM1(N), 3     80
     1 NUM2(N)                                                           3     80
   43 FORMAT (F8.3, F8.5, 2F8.3, 2I4)                                    3     81
   44 IF (ETA(N) - 3.333) 41, 47, 45                                     3     82
   45 IF (ETA(N) - 6.666) 46, 47, 46                                     3     83
   46 WRITE OUTPUT TAPE 6,17, ETA(N), TIME(N)                            3     84
  322 GO TO 1                                                            3     84A
   47 N = N-1                                                            3     85
  246 FN = N                                                             3     85A
   48 DO 50 I = 1,N                                                      3     86
   49 PHI(I) = ETA(I) - ETAZ                                             3     87
   50 TENS(I) = GMAX  - GAMMAF (PHI(I))                                  3     88
C
  150 TEST = TENS(1)                                                     3     89
   51 DO 55 I = 1,N                                                      3     90
  243 IF(AMT - 999.99) 152, 247, 152                                     3     90A
  247 FI = I                                                             3     90B
  248 AM = AM1 + (AM2 - AM1) * FI/FN                                     3     90C
  253 COA = 4.835974*((AM*.001/RHO)**(2./3.))                            3     90D
  254 Q = 0.00493164/(HGT*(AM*.001*RHO*RHO)**(1./3.))                    3     90E
  152 RATIO = BRAF (TIME(I),TENS(I))/BRAF(TSTARF(TENS(I)),TENS(I))       3     91
  153 AREA(I) = COA * RATIO *(TIME(I)**(2./3.))* 100.                    3     92
   52 CAP(I) = CAPX(I)/(AREA(I)*.01)                                     3     93
   53 RAD =.0282095*SQRTF(AREA(I))                                       3     94
   54 SOLR = DELTA*RAD/( SKAPPA*(RAD + DELTA))                           3     95
   55 RES(I) = 0.01*AREA(I)*(RESX(I)-CRES) - SOLR                        3     96
C
C       THE FIRST TIME AROUND WE PRINT THE RESULTS AND SEE IF WE ARE GO- 3     97
C     ING TO INTEGRATE. NEXT   TIME AROUND WE SKIP THAT PART.           3     98
   56 IF (NM - 1) 163, 60, 59                                            3     99
   60 WRITE OUTPUT TAPE 6, 61,(NUM1(I), NUM2(I), ETA(I), TIME(I), CAPX   3    100
```

```
 1    CAPACITY OF A DROPPING AMALGAM ELECTRODE - PROGRAM 3-                5/09/64

     1 (I), RESX(I), AREA(I), CAP(I), RES(I), I = 1, N)                    3   101
    61 FORMAT (1X,2I4, 2X, F7.3, F8.5, 5F8.3)                              3   102
   159 GO TO 63                                                            3   103
C
    59 IF(PHI(J)) 62, 73, 76                                               3   104
    62 WRITE OUTPUT TAPE 6, 94, PHI(J), J                                  3   105
   162 GO TO 1                                                             3   106
C
   163 WRITE OUTPUT TAPE 6, 164, NM                                        3   107
   164 FORMAT (/41H THE ITERATION INDEX IS LESS THAN 1, NM = I3)           3   108
   165 GO TO 1                                                             3   109
C
    63 IF (ETA(N+1) - 3.333) 65, 70, 64                                    3   110
    64 IF (ETA(N+1) - 6.666) 65, 67, 65                                    3   111
    65 WRITE OUTPUT TAPE 6, 66, ETA(N+1)                                   3   112
    66 FORMAT (/46H WE HAVE LOST THE  END-NUMBER. INSTEAD WE HAVE F8.3)    3   113
   166 GO TO 1                                                             3   114
    67 WRITE OUTPUT TAPE 6, 68, N                                          3   115
    68 FORMAT (/52H THE TEST NUMBER WAS 6.666 - NO INTEGRATION WAS DONE/   3   116
      112H THERE WERE I2, 25H DATA POINTS IN THIS SET.)                    3   117
    69 GO TO 228                                                           3   118
C49                                                                        3   119
C50    THE NEXT SEQUENCE INTEGRATES THE CAPACITY TO GIVE SURFACE CHARGE    3   120
C51    AND INTERFACIAL TENSION. J IS THE INDEX ABOVE ZERO CHARGE POINT.    3   121
    70 DO 140 I=1,N                                                        3   122
   140 PHI(I) = ETA(I) - ETAZ                                              3   123
   141 DO 72 J=1,N                                                         3   124
    71 IF (PHI(J)) 72, 73, 76                                              3   125
    72 CONTINUE                                                            3   126
    73 CAPZ = CAP(J)                                                       3   127
    74 CHG(J) = 0.                                                         3   128
    75 GO TO 78                                                            3   129
    76 CAPZ =  CAP(J)  - (CAP(J) - CAP(J-1))*PHI(J)/(PHI(J)-PHI(J-1))      3   130
    77 CHG(J) = 0.5*PHI(J)*(CAP(J) + CAPZ)                                 3   131
    78 CHG(J-1) =  0.5*PHI(J-1)*(CAPZ + CAP(J-1))                          3   132
    79 CHGZ = 0.                                                           3   133
   142 J2 = J-2                                                            3  133A
   143 J1 = J+1                                                            3  133B
    80 DO 81 I= 1, J2                                                      3   134
    81 CHG(I) =  0.5*(CAP(I) + CAP(I+1))*(PHI(I) - PHI(I+1))               3   135
    82 DO 83 I= J1 ,N                                                      3   136
    83 CHG(I) =  0.5*(CAP(I) + CAP(I-1))*(PHI(I) - PHI(I-1))               3   137
    84 K = J-1                                                             3   138
    85 K = K-1                                                             3   139
    86 CHG(K) = CHG(K) + CHG(K+1)                                          3   140
    87 IF (K -1) 88,88,85                                                  3   141
    88 K = J                                                               3   142
    89 K = K+1                                                             3   143
    90 CHG(K) = CHG(K) + CHG(K-1)                                          3   144
    91 IF (K-N) 89,92,92                                                   3   145
C53                                                                        3   146
C54    WE HAVE THE CHARGE. WE INTEGRATE AGAIN TO GET INTERFACIAL TENSION.  3   147
    92 IF (PHI(J)) 93,98,98                                                3   148
    93 WRITE OUTPUT TAPE 6, 94, PHI(J), J                                  3   149
    94 FORMAT (/30H PHI(J) IS NEGATIVE,AND EQUALS F5.3, 5H J = I2)         3   150
    95 GO TO 1                                                             3   151
```

```
C
   98 TENS(J) = GMAX - 5.0*PHI(J)*CHG(J)                                3   152
   99 TENS(J-1) = GMAX - 5.0*PHI(J-1)*CHG(J-1)                          3   153
  100 DO 101 I = 1, J2                                                  3   154
  101 TENS(I) = 5.0*(CHG(I)+ CHG(I+1))*(PHI(I) - PHI(I+1))              3   155
  102 DO 103 I = J1 ,N                                                  3   156
  103 TENS(I) = 5.0*(CHG(I)+ CHG(I-1))*(PHI(I) - PHI(I-1))              3   157
  104 K = J-1                                                           3   158
  105 K = K-1                                                           3   159
  106 TENS(K) = TENS(K+1) - TENS(K)                                     3   160
  107 IF (K-1) 108, 108, 105                                            3   161
  108 K = J                                                             3   162
  109 K = K+1                                                           3   163
  110 TENS(K) = TENS(K-1) - TENS(K)                                     3   164
  111 IF (K-N) 109,112,112                                              3   165
C
C        WHEN THERE IS NO AREA CALCN, WE SKIP THE 2ND APPROX. FOR TENS.  3   166
  112 IF (RHO - 99.999)  167, 120, 115                                  3   167
  115 WRITE OUTPUT TAPE 6, 116                                          3   168
  116 FORMAT (/ 7H RHO IS F8.3, 28H WHICH IS LARGER THAN 99.999)        3   169
  323 GO TO 1                                                           3   170
  167 IF (ABSF(TEST - TENS(1))-  0.01)  113,113, 168                    3   171
  168 NM =NM+1                                                          3   172
  169 GO TO 125                                                         3   173
C                                                                       3   174
  113 WRITE OUTPUT TAPE 6, 2                                            3  174A
  402 WRITE OUTPUT TAPE 6, 114                                          3   175
  114 FORMAT(//60H      SECOND APPROX.  BASED ON INTEGRATED INTERFACIAL T 3   176
     1ENSION  //66H    RUN      POT       INT.TENS.--ERG/SQ.CM     AREA    C 3   177
     2AP   POL-RES /66H   NO.     VOLTS     ASSUMED  INTEGRATED      SQ MM  3   178
     3 MF/SQCM  OHM-CM2/)                                               3   179
C                                                                       3   180
  170 WRITE OUTPUT TAPE 6, 171,(NUM1(I), NUM2(I), ETA(I), ATENS(I),     3   181
     1 TENS(I), AREA(I), CAP(I), RES(I), I = 1, N)                      3   182
  171 FORMAT (1X,2I4, 2X, F7.3, 3X, 2F8.2, 5X, 3F8.3)                   3   183
  172 WRITE OUTPUT TAPE 6, 173, CAPZ, N, NM, J                          3   184
  173 FORMAT (//42H THE CAPACITY AT THE ZERO CHARGE POINT IS F8.3/12H TH 3   185
     1ERE WERE I2,25H DATA POINTS IN THIS SET./56H TO ACHIEVE A PRECISIO 3   186
     2N OF 0.01  IN INT.TENSION REQUIRED I3,12H ITERATIONS./4H J= I2)    3   187
  308 WRITE OUTPUT TAPE 6, 35, DIAM, M                                  3  187A
C60                                                                     3   188
C61    THE NEXT PART OF THE PROGRAM CALCULATES THE CONTRIBUTION TO THE  3   189
C62    CAPACITY FROM THE DIFFUSE (GOUY) AND COMPACT (HELMHOLTZ) DOUBLE  3   190
C63    LAYERS,AS WELL AS THE INTEGRAL CAPACITIES.                       3   191
C64                                                                     3   192
  120 DO 178  I=1,N                                                     3   193
  178 CAPINT (I) = CHG(I)/PHI(I)                                        3   194
  174 FJ = J                                                            3   195
  175 DO 177 I =1,N                                                     3   196
  176 FI = I                                                            3   197
  177 PSI(I) = 0.005*(FJ - FI)                                          3   198
  181 W = 11.72 *SQRTF(CONC*(TEMP+273.16)/298.16)                       3   201
  182 V = 19.46 *298.16/(TEMP + 273.16)                                 3   202
C
  183 DO 191 I =1,N.                                                    3   203
  184 F = CAPINT(I)* (PHI(I)-PSI(I)) - W*SINHF(V*PSI(I))                3   204
```

```
1    CAPACITY OF A DROPPING AMALGAM ELECTRODE - PROGRAM 3-                    5/09/64

  185 G = -CAPINT(I) - W*V*COSHF(V*PSI(I))                          3   205
  186 PSI1 = PSI(I) -(F/G)                                          3   206
  187 IF (ABSF(PSI1 - PSI(I)) - 0.001) 190,190,188                  3   207
  188 PSI(I) = PSI1                                                 3   208
  189 GO TO 184                                                     3   209
  190 PSI(I) = PSI1                                                 3   210
  191 CAPIG(I) = W*SINHF(V*PSI(I))/PSI(I)                           3   211
  193 NN =1                                                         3   212
  192 TEST2 = CAPIG(I)                                              3   213
      DO 205  I=1,N                                                 3   214
  195 CAPIH(I) = 1./((1./CAPINT(I)) - (1./CAPIG(I)))                3   215
C
C69   WITH THIS IMPROVED HELMHOLTZ INTEGRAL CAPACITY, BASED ON THE   3   216
C70   EXPERIMENTAL RESULTS, WE GET A BETTER VALUE FOR PSI.           3   217
  197 F = CAPIH(I)*(PHI(I) - PSI(I)) - W*SINHF(V*PSI(I))            3   218
  198 G = -CAPIH(I) - W*V*COSHF(V*PSI(I))                           3   219
  199 PSI1 = PSI(I) -(F/G)                                          3   220
  200 IF(ABSF(PSI1 - PSI(I)) -.0001) 203,203,201                    3   221
  201 PSI(I) = PSI1                                                 3   222
  202 GO TO 197                                                     3   223
  203 PSI(I) = PSI1                                                 3   224
  205 CAPIG(I) = W*SINHF(V*PSI(I))/PSI(I)                           3   225
  206 IF (ABSF(CAPIG(1) - TEST2) - .01)  209,209,207                3   226
  207 NN = NN +1                                                    3   227
  208 GO TO 192                                                     3   228
C71                                                                 3   229
  209 U = 228.5*SQRTF(CONC*298.16/(TEMP+273.16))                    3   300
  210 DO 212 I = 1,N                                                3   301
  211 CAPG(I) = U*COSHF(V*PSI(I))                                   3   302
  212 CAPH(I) = 1./(1./CAP(I) -1./CAPG(I))                          3   303
C
  403 WRITE OUTPUT TAPE 6, 2                                        3  303A
  213 WRITE OUTPUT TAPE 6,214                                       3   304
  214 FORMAT(//61H RUN      POT.  RAT.POT.  PSI   DIF.CAP  INT.CAP  CHG   3   305
     1   TENS/65H  NO.     VOLTS   VOLTS   VOLTS  MF/SQCM  MF/SQCM MC/SQC 3   306
     2M ERG/SQCM /)                                                 3   307
  215 WRITE OUTPUT TAPE 6, 216, (NUM1(I), NUM2(I), ETA(I), PHI(I),  3   308
     1 PSI(I), CAP(I), CAPINT(I), CHG(I), TENS(I), I = 1,N)         3   309
  216 FORMAT ( 1X,214, 3F8.3, 4F8.2)                                3   310
  217 WRITE OUTPUT TAPE 6,218, ETAZ, CHGZ,CHGZ, CAPZ,CAPZ, CHGZ, GMAX  3   311
  218 FORMAT (/4H ECM 4X, 3F8.3,  4F8.2)                            3   312
C
  404 WRITE OUTPUT TAPE 6, 2                                        3  312A
  219 WRITE OUTPUT TAPE 6, 220                                      3   313
  220 FORMAT(//57H RUN   RAT.POT  TOTAL CAPACITY    HELMHOLTZ        DIFF 3   314
     1USE/62H  NO.    VOLTS   DIFF.    INT.   DIFF.    INT.    DIFF.   I 3   315
     2NT./)                                                         3   316
  221 WRITE OUTPUT TAPE 6, 222, (NUM1(I), NUM2(I), PHI(I), CAP(I),  3   317
     1 CAPINT(I), CAPH(I), CAPIH(I), CAPG(I), CAPIG(I), I = 1,N)    3   318
  222 FORMAT ( 1X,214, F8.3, 6F8.2)                                 3   319
  223 WRITE OUTPUT TAPE 6, 224, N, NN                               3   320
  224 FORMAT(//12H THERE WERE I2, 25H DATA POINTS IN THIS SET./55H TO AC 3   321
     1HIEVE A PRECISION OF .01 IN THE INTEGRAL CAPACITY/39H OF THE HELMH 3   322
     2OLTZ DOUBLE LAYER REQUIRED I3,12H ITERATIONS.)                3   323
C
  228 WRITE OUTPUT TAPE 9, 2                                        3   324
```

```
1     CAPACITY OF A DROPPING AMALGAM ELECTRODE - PROGRAM 3-                  5/09/64

 225 WRITE OUTPUT TAPE 9,  21, (ETA(I), CAP(I), NUM(I), I=1,N)          3   325
 227 GO TO 1                                                            3   326
     END(1,1,0,0,0,0,1,1,0,0,0,0,0,0,0)
```

FORMS FOR INPUT DATA TO PROGRAM 3

The information which must appear on successive cards, and the form in which it must appear, is described below:

CARD 1:

Column 1: A "1" or "2" must appear in column one. This signals the beginning of a new data set. A "1" sets the printer at the top of a new page when the output is printed. A "2" causes the printer to begin at the next half-page.

Columns 2-80: This space is allowed for a title.

CARD 2:

Columns 1-8: RHO, the density of the amalgam, g/cm^3. Three decimal places.

Columns 9-16: HGT, the height of the reservoir above the capillary tip, cm. Three decimal places.

Columns 17-24: AM, the mass flow rate, mg/sec. Three decimal places.

Columns 25-32: DELTA, the radius of the cylindrical or spherical counter electrode surrounding the drop. Three decimal places.

Columns 33-40: TEMP, the temperature, ^{o}C. Two decimal places.

CARD 3:

Columns 1-8: GMAX, the maximum interfacial tension, erg/cm^2 (or dyne-cm). Two decimal places. This value determines the absolute value of the calculated interfacial tension.

Columns 9-16: ETAZ, the potential of zero charge, volts. Three decimal places. The potential is given with respect to the same reference electrode as was used in the capacity measurements. This value can often be determined as the zero-current point during the capacity measurements [15, 16]. For mercury in solutions with little specific adsorption, the zero charge potential is - 0.192 volts vs. a standard H_2 electrode [1, 2].

Columns 17-24: CONC, the concentration of 1-1 electrolyte, moles/liter. Five decimal places. For 1-2 or other types of electrolytes, the last part of the program must be modified, since the equations used to calculate properties of the diffuse double layer are different [8].

Columns 25-32: SKAPPA, the specific conductance of the electrolyte, $ohm^{-1}cm^{-1}$. Five decimal places.

Columns 33-40: CRES, the resistance of the amalgam thread in the capillary, ohms. Three decimal places.

CARD 4:

Columns 1-8: CAPO, K_o in equation (6), $\mu f/cm^2$. Three decimal places.

Columns 9-16: CAP1, K_1 in equation (6), $\mu f \ cm^{-2} \ volt^{-1}$. Three decimal places.

Columns 17-24: CAP2, K_2 in equation (6), $\mu f \ cm^{-2} \ volt^{-2}$. Three decimal places.

This completes the input of parameters. The next group of cards, from 1 to 79 in number, contains data on drop lifetime measured at various potentials. The data should appear in the following form. The last card marks the end of this data set.

DROP LIFETIME CARDS:

Columns 1-8: ETA1 (M), potential, volts. Three decimal places.

Columns 9-16: T1 (M), time, seconds. Five decimal places.

LAST CARD:

Columns 1-8: 0003.333

The next group of cards contains the actual data. There may be up to 79 of these. The last card marks the end of the data set, and provides an option to terminate the calculation before performing the integration.

CAPACITY DATA CARDS:

Columns 1-8: ETA (N), potential, volts. Three decimal places.

Columns 9-16: TIME (N), time, seconds. Five decimal places.

Columns 17-24: CAPX (N), experimental value of capacity, microfarads. Three decimal places.

Columns 25-32: RESX (N), experimental value of resistance, ohms. Three decimal places.

Columns 33-40: NUM (N), identification number consisting of up to eight numerical digits.

LAST CARD:

Columns 1-8: 0003.333

This will cause the calculation to run to completion, producing a printed output containing the capacity, polarization resistance, integrated values of surface charge, interfacial tension, integral capacity, and the capacities of the Helmholtz and diffuse double layers.

ALTERNATE LAST CARD:

Columns 1-8: 0006.666

This will cause the calculation to terminate on completing the calculations of capacity and polarization resistance. In addition to the printed output, cards will be punched in the correct format for completing the integrations at a later time.

In addition to the direct path and terminated path described above, the program provides two other alternatives (Fig. 1).

MASS FLOW INTERPOLATION

If the mass flow rate is not constant throughout a series of measurements, a linear interpolation of mass flow rate can be used. If this desired,

the field (Columns 17-24) for AM on card 2 should read 0999.990. Card 2 should then be followed by an additional card:

INTERPOLATION CARD:

Columns 1-8: AM1, initial value of mass flow rate, mg/sec. Three decimal places.

Columns 9-16: AM2, final value of mass flow rate, mg/sec. Three decimal places.

Card 3 should follow this card. The rest of the data input is the same as above. The calculation may be terminated without integration by the alternate last card.

INTEGRATION FROM PRE-CALCULATED CAPACITY DATA:

If the calculation has been terminated without integration in a previous run, or if data from several calculations, or from the literature, are to be combined for integration, the first part of the calculation can be skipped over. If this is desired, the data input should be in the following form:

CARD 1:

Column 1: A "1" must appear in column 1.

Columns 2-80: Title

CARD 2:

Columns 1-8: This field should read 0099.999.

Columns 9-32: These may be blank or may contain the same data as for the main program. Numbers appearing in these fields will not be used in the calculations.

Columns 33-40: TEMP, the temperature, ^{o}C. Two decimal places.

CARD 3:

Columns 1-8: GMAX, the maximum interfacial tension, erg/cm^2. Two decimal places.

Columns 9-16: ETAZ, the potential of zero charge, volts. Three decimal places.

Columns 17-24: CONC, the concentration of 1-1 electrolyte, moles/liter. Five decimal places.

Columns 25-40: These may be blank, or may contain the same data as the main program. Numbers appearing in these fields will not be used in the calculations.

The fourth card, containing parameters for the trial capacity function, (equation 6) is not needed, and should be left out.

CAPACITY DATA CARDS:

Columns 1-8: ETA (N), potential, volts. Three decimal places.

Columns 9-16: blank

Columns 17-24: CAP (N), capacity, $\mu f/cm^2$. Two decimal places.

Columns 25-32: blank

Columns 33-40: NUM (N), identification number consisting of up to eight numerical digits.

LAST CARD:

Columns 1-8: 0003.333

With this set of input data, the program will be entered at the point where the integrations are to be performed, and will skip the calculations of the area and capacity. If it is possible to obtain a complete set of capacity data for integration directly from the experimental results, this should be done. If the capacity is calculated in one run, and the integrations are performed in the next run, some loss of accuracy results. This inaccuracy occurs because the drop area is calculated using only the trial function for interfacial tension, not the values obtained by integrating the capacity. In a typical case, dividing the calculation this way would introduce an error of

about one percent in the calculated capacity values, and a larger, cumulative error in the quantities obtained by integration which might be as large as 5%.

Examples of input and output data follow .

2 CAPACITY AMALGAM 8 IN 30.4 AT.1RC BOOK 77 PAGE 661					
11.66	45.	999.99	1.6	25.	77 66 1
12.55	11.38				77 66 1
459.5	-.45	.1	.0385		77 66 1
41.5	114.	134.			77 66 1
-1.1	.278	77 6612			
-1.0	.281	77 6613			
-.9	.278	77 6614			
-.8	.300	77 6615			
-.7	.308	77 6616			
-.6	.320	77 6617			
-.5	.330	77 6618			
-.45	.299	77 6619			
3.333					
-1.1	.214	.3	224.	77 6612	
-1.0	.134	.2	160.	77 6613	
-.9	.217	.3	80.	77 6614	
-.8	.200	.3	84.	77 6615	
-.7	.157	.3	90.	77 6616	
-.6	.259	.6	68.	77 6617	
-.5	.203	.6	78.	77 6618	
-.45	.157	.6	82.	77 6619	
3.333					

CAPACITY AMALGAM 8 IN 30.4 AT.1KC BOOK 77 PAGE 661

RHO =	11.660	GMAX =	459.50	CAP0 =	41.500
HGT =	45.000	ETAZ =	-0.450	CAP1 =	114.000
FLOW =	999.990	CONC =	0.10000	CAP2 =	134.000
DELTA=	1.600	KAPPA =	0.038500	TEMP =	25.00
CRES =	-0.				

THE MASS FLOW RATE USED IS A LINEAR INTERPOLATION BETWEEN
AM1 = 12.550 AND AM2 = 11.380

DROP LIFETIME DATA

POT	TIME	GAMMA	DIA
-1.100	0.27800	416.39	0.00258
-1.000	0.28100	429.30	0.00250
-0.900	0.27800	438.37	0.00240
-0.800	0.30000	445.35	0.00252
-0.700	0.30800	451.16	0.00252
-0.600	0.32000	455.94	0.00256
-0.500	0.33000	459.03	0.00259
-0.450	0.29900	459.50	0.00231

AVERAGE DIAMETER OF CAPILLARY = 0.00250 MILLIMETERS
NUMBER OF MEASUREMENTS = 8

CAPACITY AMALGAM 8 IN 30.4 AT.1KC BOOK 77 PAGE 661

FIRST APPROXIMATION BASED ON ASSUMED INTERFACIAL TENSION

RUN NO.	POT VOLTS	TIME SEC	EXP-CAP M-FARADS	EXP-RES OHMS	AREA SQ MM	CAP MF/SQCM	POL-RES OHM-CM2
7706612	-1.100	0.21400	0.300	224.000	1.797	16.694	3.066
7706613	-1.000	0.13400	0.200	160.000	1.293	15.462	1.253
7706614	-0.900	0.21700	0.300	80.000	1.783	16.824	0.471
7706615	-0.800	0.20000	0.300	84.000	1.672	17.942	0.478
7706616	-0.700	0.15700	0.300	90.000	1.404	21.362	0.413
7706617	-0.600	0.25900	0.600	68.000	1.961	30.602	0.332
7706618	-0.500	0.20300	0.600	78.000	1.645	36.465	0.364
7706619	-0.450	0.15700	0.600	82.000	1.368	43.869	0.282

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SECOND APPROX. BASED ON INTEGRATED INTERFACIAL TENSION

RUN NO.	POT VOLTS	INT.TENS.--ERG/SQ.CM ASSUMED	INTEGRATED	AREA SQ MM	CAP MF/SQCM	POL-RES OHM-CM2
7706612	-1.100	416.39	402.36	1.798	16.688	3.067
7706613	-1.000	429.30	416.44	1.294	15.452	1.254
7706614	-0.900	438.37	428.91	1.784	16.820	0.471
7706615	-0.800	445.35	439.71	1.672	17.941	0.478
7706616	-0.700	451.16	448.65	1.404	21.363	0.413
7706617	-0.600	455.94	455.31	1.960	30.608	0.332
7706618	-0.500	459.03	459.00	1.645	36.472	0.364
7706619	-0.450	459.50	459.50	1.367	43.878	0.282

THE CAPACITY AT THE ZERO CHARGE POINT IS 43.878
THERE WERE 8 DATA POINTS IN THIS SET.
TO ACHIEVE A PRECISION OF 0.01 IN INT.TENSION REQUIRED 2 ITERATIONS.
J= 8

AVERAGE DIAMETER OF CAPILLARY = 0.00253 MILLIMETERS
NUMBER OF MEASUREMENTS = 8

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RUN NO.	POT. VOLTS	RAT.POT. VOLTS	PSI VOLTS	DIF.CAP MF/SQCM	INT.CAP MF/SQCM	CHG MC/SQCM	TENS ERG/SQCM
7706612	-1.100	-0.650	-0.108	16.69	22.90	-14.89	402.36
7706613	-1.000	-0.550	-0.102	15.45	24.14	-13.28	416.44
7706614	-0.900	-0.450	-0.096	16.82	25.92	-11.66	428.91
7706615	-0.800	-0.350	-0.088	17.94	28.36	-9.93	439.71
7706616	-0.700	-0.250	-0.077	21.36	31.94	-7.96	448.65
7706617	-0.600	-0.150	-0.060	30.61	35.75	-5.36	455.31
7706618	-0.500	-0.050	-0.027	36.47	40.17	-2.01	459.00
7706619	-0.450	-0.	0.	43.88	-0.	0.	459.50
ECP	-0.450	0.	0.	43.88	43.88	0.	459.50

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RUN NO.	RAT.POT VOLTS	TOTAL CAPACITY DIFF.	INT.	HELMHOLTZ DIFF.	INT.	DIFFUSE DIFF.	INT.
7706612	-0.650	16.69	22.90	17.67	27.46	299.07	138.02
7706613	-0.550	15.45	24.14	16.39	29.65	268.77	129.96
7706614	-0.450	16.82	25.92	18.10	32.93	238.62	121.77
7706615	-0.350	17.94	28.36	19.65	37.88	206.58	112.87
7706616	-0.250	21.36	31.84	24.41	46.15	171.21	102.74
7706617	-0.150	30.61	35.75	40.32	59.50	127.10	89.58
7706618	-0.050	36.47	40.17	65.57	86.00	82.19	75.40
7706619	-0.	43.88	-0.	111.71	-0.	72.26	0.

THERE WERE 8 DATA POINTS IN THIS SET.
TO ACHIEVE A PRECISION OF .01 IN THE INTEGRAL CAPACITY
OF THE HELMHOLTZ DOUBLE LAYER REQUIRED 5 ITERATIONS.

APPENDIX II

Figure 2 - oscilloscope trace showing points read.

Figure 3 - Format for cards punched by graph reader.

Listing of Program 4.

Text describing input data to Program 4.

Sample data.

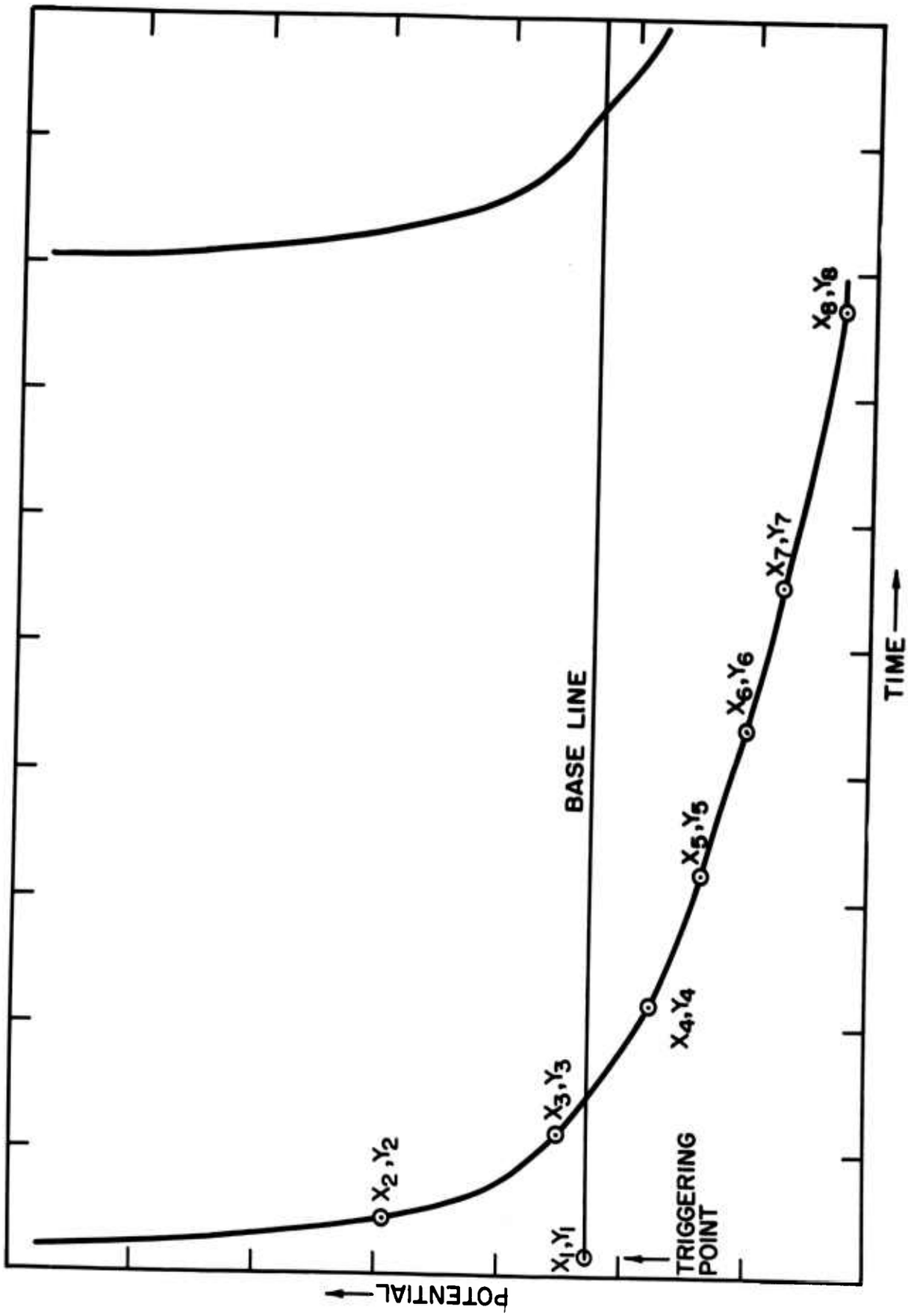

FIG. 2 Oscilloscope trace showing points read.

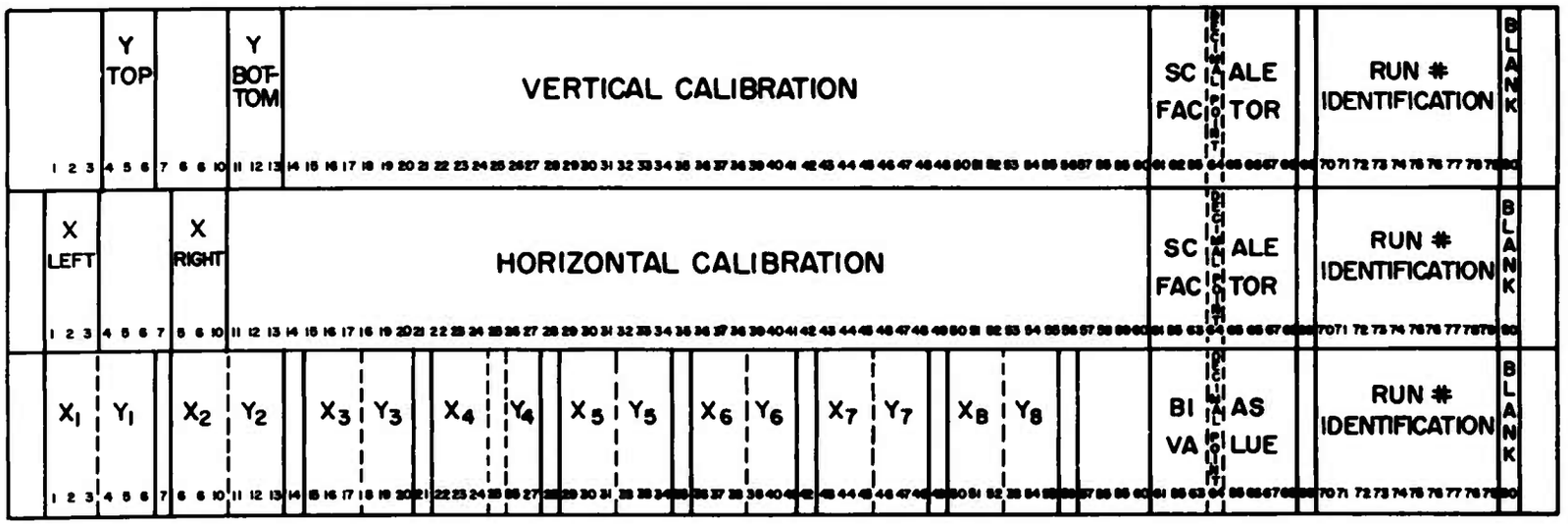

FIG. 3 Format for cards punched by graph reader.

```
C      DR. JAMES N. BUTLER - APRIL 1964       PROGRAM  4
C      THIS PROGRAM TAKES DATA FROM THE GERBER A-D CONVERTER AND MAKES
C        THE CALCULATIONS TO GET CURRENT DENSITY AND OVERVOLTAGE.
       DIMENSION KX(8), KY(8), X(8), Y(8), U(8), TIME(8), AREA(8), ETA(8)
       DIMENSION CD(8), CDO(8), TITLE(20) , NUM(3), NUMB(3), NUM1(3)
    1  READ 101, DELTA, COND
   35  READ 111, TITLE
   36  TYPE 111, TITLE
   37  PUNCH 111, TITLE
    2  READ 102, RHO
    5  N = 0
   77  DO 78 I = 1,3
   78  NUM1(I) = 0
   79  N1 = 0
    6  READ 105,KX(1),KY(1),KX(2),KY(2),KX(3),KY(3),KX(4),KY(4),KX(5),
      1KY(5),KX(6),KY(6),KX(7),KY(7),KX(8),KY(8), BIAS,NUM, M
   38  IF (M - 8) 50, 39, 34
   39  KYV1 = KY(1)
   40  KYV2 = KY(2)
   41  VSCA = BIAS
   43  GO TO 6
   34  IF (KX(1) - 998) 45, 62, 222
   62  TYPE 108, NUM1, N1
   63  IF (KX(1) - 998)  1, 1, 222
   45  KXH1 = KX(1)
   46  KXH2 = KX(2)
   47  HSCA = BIAS
   49  GO TO 6
   50  IF(M) 11, 11, 14
   11  IF (KX(1) - 998) 14, 12, 12
   12  TYPE 108, NUM1, N1
   13  IF ( KX(1) - 998 ) 35, 35, 222
   14  N = N+1
    7  READ 104, CURR, AM, NUMB, NB
    8  IF (NUM(3) - NUMB(3))  9, 54, 9
    9  TYPE 107, NUM, NUMB
   51  GO TO 6
   54  IF (M - NB) 55, 16, 55
   55  TYPE 107, M, NB
   10  GO TO 6
   16  YV = KYV1 - KYV2
   17  XH = KXH2 - KXH1
   82  DO 80 I = 1, 3
   80  NUM1(I) = NUM(I)
   81  N1 = N
   30  PUNCH 109, NUM, CURR
   18  DO 29 I = 2, 8
   70  IF (KX(I)) 85, 85, 71
   71  IF (KY(I)) 85, 85, 19
   85  K = I - 1
   86  GO TO 31
   19  Y(I) = KY(I) - KY(1)
   20  X(I) = KX(I) - KX(1)
   21  U(I) = BIAS + (VSCA * Y(I)/ YV)
   22  TIME (I) = HSCA * X(I)/ XH
   23  AREA(I) = 4.83597 * ((AM * .001 * TIME(I) / RHO)**(2./3.))
   24  RAD = 0.282095 * SQRTF (AREA(I))
   28  AREA (I) = 100. * AREA(I)
   25  CD(I) = CURR* .0001/ AREA(I)
```

```
 26 VIR = CD(I) * DELTA * RAD / (COND*(RAD + DELTA))
 27 ETA(I) = U(I) - VIR
 29 CDO(I) = -0.434294 * LOGF(CD(I)) + 8.543*ETA(I)
 87 K = 8
 31 DO 53 I = 2, K
 53 PUNCH 106, CD(I), ETA(I), NUM, M
 66 DO 32  I = 2,K
 65 CD(I) = 1000. * CD(I)
 32 PUNCH 110, U(I), TIME(I), AREA(I), ETA(I), CD(I), CDO(I)
 33 GO TO 6
222 CALL EXIT
101 FORMAT (F8.3, F8.5)
102 FORMAT (F8.3)
104 FORMAT (F10.4, F8.4, 51X, 3I3, I1)
105 FORMAT (I3,I3,1X,I3,I3,1X,I3,I3,1X,I3,I3,1X,I3,I3,1X,I3,I3,1X,I3,I
   13,1X,I3,I3,5X,F8.4,1X,3I3, I1)
106 FORMAT (F10.8, F8.4, 51X, 3I3, I1)
107 FORMAT(/40H THE I.D.NUMBER ON THE PICTURE CARD IS  3I3/ 36H THE NU
   1MBER ON THE CURRENT CARD IS  3I3/ 19H THEY DO NOT AGREE.)
108 FORMAT(/31H THE DATA SET ENDING WITH RUN  3I3, 13H IS FINISHED./
   114H IT CONTAINED I3,15H PICTURE CARDS.)
109 FORMAT(/24H ---------- RUN NUMBER  3I3,9X,F10.3,10H MICROAMP.//48H
   1      U     TIME      AREA     ETA    CURR DENS ROUGH    /            50H
   2    VOLTS   SEC.      SQ MM   VOLTS   MA/SQ CM  -LOG IO /)
110 FORMAT (F8.3,F10.5, F6.3, F8.3, F10.4, F8.3)
111 FORMAT (20A4)
    END
```

FORMS FOR INPUT DATA TO PROGRAM 4

The format in which the cards are punched is shown in Fig. 3. The vertical calibration is identified by an 8 in column 79; the horizontal calibration is identified by a 9 in column 79; the other columns of the identification number (columns 70 to 78) are used to identify the picture from which the data was read.

The scale factor in the vertical calibration is the actual potential difference in volts between two calibration marks, y_{top} and y_{bottom}. The scale factor in the horizontal calibration is the actual time difference in seconds between two calibration marks, x_{left} and x_{right}.

The third type of card contains the actual data read from the potential-time curve. The first point is a reference point, taken at the bias voltage, at the time corresponding to the initial point of the curve (triggering point in Fig. 2); the remaining 7 points may be anywhere on the curve. The bias voltage (potential of the base line) is also included on this card.

The remaining data required to do the calculations is summarized below. This is the order in which the cards must appear:

CARD 1:

Columns 1-8: DELTA, the diameter of the cylindrical screen surrounding the drop, cm. Three decimal places.

Columns 9-16: COND, the specific conductance of the electrolyte, $ohm^{-1}cm^{-1}$. Five decimal places.

CARD 2:

Column 1: A "1" must appear in column 1.

Columns 2-80: This space is for a title.

CARD 3:

Columns 1-8: RHO, the density of the amalgam, g/cm^3. Three decimal places.

CARD 4:

A vertical calibration card (See Fig. 3). "8" must appear in column 79.

CARD 5:

A horizontal calibration card (See Fig. 3). "9" must appear in column 79.

CARD 6:

A picture-curve card (See Fig. 3). Column 79 may contain any digit from 1 to 7.

CARD 7:

Columns 1-10: CURR, current, microamperes. Four decimal places.

Columns 11-18: AM, mass flow rate, mg/sec. Four decimal places.

Columns 70-79: Run identification number. This number must agree exactly with the corresponding number on the picture card (card 6).

There may follow any number of cards of type 6, each followed by one of type 7.

The horizontal or vertical calibration is changed by inserting a new card of type 4 or 5 before the next card of type 6.

A new set of data is started by a card containing "998" in columns 1-3, followed by cards of type 2, 3, 4, 5, 6, and 7.

Ordinarily, the diameter of the screen and the conductance of the solution are constant throughout any set of calculations. However, if it is desired to change the value of DELTA and COND, the card before the new set of data should contain "998" in columns 1-3 and "9" in column 79. This should be followed by cards of types 1, 2, 3, 4, 5, 6, and 7.

The last card of the calculation should contain "999" in columns 1-3.

This program was written for an IBM 1620 computer which produced only punched-card output. It was necessary to separate the output for printing (PUNCH statement 32) from that which was provided for input to Program 5, which performs a least-squares analysis on the data (PUNCH statement 53). This is facilitated by the numbers punched in columns 70-79.

```
 MAY 13, 1964    PROGRAM 4
DATA

  1.6     .0385          DELTA, COND FOR 0.1 M HCLO4

1 THALLIUM AMALGAM NO. 8 5-5-64  BOOK 96 PAGES 43 RUNS 1-21.  41.16 MOLE PCT.

  12.715          RHO FOR AMALGAM 8 THALLIUM

   495    213                                                        .2000 0960430218
063    622                                                          .4000 0960430209
032284 047310 069260 112213 196175 265156 331143 419130      001.3000 0960430021
  130.       3.675                                                     96 43  21
436285 450314 471260 500225 538198 592176 645161 736143      001.3000 0960430032
  131.       3.675                                                     96 43  32
391286 411294 442240 502199 563175 640158 717146             001.2900 0960430 42
  118.       3.675                                                     96 43  42
032290 069298 108262 153240 210221 293201 368189 478172      001.2200 0960430061
   60.       3.675                                                     96 43  61
248    599                                                          .5000 0960430199
390282 436323 483292 543273 603256 695241                    001.0500 0960430092
    7.02     3.675                                                     96 43  92
999
```

MAY 13, 1964 PROGRAM 4
PRINTED OUTPUT

U VOLTS	TIME SEC.	AREA SQ MM.	ETA VOLTS	CURR DENS MA/SQ CM	ROUGH -LOG IO
---------- RUN NUMBER 96 43 2					130.000 MICROAMP.
1.318	.01073	.102	1.288	126.3783	11.909
1.282	.02647	.187	1.261	69.2254	11.933
1.249	.05724	.314	1.232	41.4006	11.914
1.222	.11735	.506	1.209	25.6549	11.923
1.209	.16672	.640	1.197	20.3000	11.922
1.200	.21395	.756	1.189	17.1904	11.924
1.190	.27692	.898	1.180	14.4741	11.927
---------- RUN NUMBER 96 43 3					131.000 MICROAMP.
1.320	.01001	.098	1.290	133.3448	11.896
1.282	.02504	.180	1.259	72.3906	11.903
1.257	.04579	.270	1.239	46.4106	11.901
1.238	.07298	.369	1.222	35.4608	11.895
1.222	.11162	.490	1.209	26.7287	11.902
1.212	.14955	.595	1.199	21.9936	11.907
1.199	.21466	.757	1.188	17.2841	11.915
---------- RUN NUMBER 96 43 4					118.000 MICROAMP.
1.295	.01431	.124	1.271	94.6932	11.884
1.257	.03649	.232	1.239	50.7331	11.884
1.228	.07942	.390	1.214	30.2081	11.896
1.211	.12307	.523	1.199	22.5590	11.893
1.199	.17817	.669	1.188	17.6281	11.909
1.190	.23327	.801	1.181	14.7296	11.922
---------- RUN NUMBER 96 43 6					60.000 MICROAMP.
1.225	.02647	.187	1.215	31.9501	11.880
1.200	.05438	.303	1.192	19.7726	11.889
1.184	.08658	.413	1.177	14.5016	11.900
1.171	.12737	.535	1.165	11.2114	11.904
1.156	.18676	.690	1.151	8.6865	11.899
1.148	.24042	.817	1.143	7.3403	11.903
1.136	.31914	.987	1.131	6.0774	11.886
---------- RUN NUMBER 96 43 9					7.020 MICROAMP.
1.079	.06552	.343	1.078	2.0430	11.900
1.057	.13247	.549	1.056	1.2777	11.918
1.043	.21794	.765	1.043	.9169	11.948
1.031	.30341	.954	1.031	.7354	11.941
1.020	.43447	1.212	1.020	.5788	11.955

MAY 13, 1964 PROGRAM 4
PUNCHED OUTPUT

.12637832	1.2889	96	43	21
.06922540	1.2611	96	43	21
.04140062	1.2328	96	43	21
.02565493	1.2094	96	43	21
.02030001	1.1974	96	43	21
.01719040	1.1892	96	43	21
.01447414	1.1808	96	43	21
.13334480	1.2901	96	43	32
.07239068	1.2598	96	43	32
.04841069	1.2391	96	43	32
.03548088	1.2226	96	43	32
.02672872	1.2091	96	43	32
.02199364	1.1997	96	43	32
.01728412	1.1884	96	43	32
.09469320	1.2713	96	43	42
.05073318	1.2395	96	43	42
.03020810	1.2146	96	43	42
.02255900	1.1994	96	43	42
.01762812	1.1888	96	43	42
.01472969	1.1811	96	43	42
.03195018	1.2156	96	43	61
.01977268	1.1922	96	43	61
.01450166	1.1777	96	43	61
.01121144	1.1651	96	43	61
.00868655	1.1516	96	43	61
.00734032	1.1435	96	43	61
.00607740	1.1319	96	43	61
.00204304	1.0782	96	43	92
.00127779	1.0564	96	43	92
.00091690	1.0430	96	43	92
.00073541	1.0310	96	43	92
.00057887	1.0204	96	43	92

APPENDIX III

Listing of Program 5.

Text describing input data for Program 5.

Sample data.

```
C      JAMES N BUTLER, TYCO LABS, APRIL 1964        PROGRAM 5
C      HYDROGEN OVERVOLTAGE, FRUMKIN CORRECTION
C        LEAST SQUARES EVALUATION OF EXCHANGE CURRENT AND TRANSFER COEFFICIENT
       DIMENSION ETA (100), CD(100), X(100), Y(100)
       DIMENSION N1(100), N2(100),N3(100),  TITLE(20), NM(100)
     1 READ 2, TITLE
     3 TYPE 2, TITLE
     4 PUNCH 2, TITLE
     5 READ 6, TEMP, CONC, ETAZ, CAP0, CAP1, CAP2
     7 PUNCH 8,TEMP, CONC, ETAZ, CAP0, CAP1, CAP2
    11 PUNCH 12
C
    10 K = 0
    13 K = K + 1
    14 READ 15, CD(K), ETA(K), N1(K), N2(K), N3(K), NM(K)
    16 IF (CD(K)) 19, 19, 13
    19 K = K - 1
C
    23 W = 5039./(TEMP + 273.16)
    24 V = 5802.5/(TEMP + 273.16)
    25 Z = 0.34005 * SQRTF (CONC * (TEMP + 273.16))
C
    26 DO 50 I = 1,K
    28 PHI0 = - ETA(I) + ETAZ
    29 CAP = CAP0 + (CAP1 * PHI0) + (CAP2 * PHI0* PHI0)
    30 P = PHI0 * CAP
C23       THE PSI-EQUATION IS SOLVED BY ITERATION USING NEWTON'S METHOD
    31 PSI = -0.05
    32 F = CAP * PSI - P + Z*(EXPF (V*PSI) - EXPF (-V*PSI))
    33 G = CAP + Z*V*(EXPF (V*PSI) + EXPF (-V*PSI))
    34 H = PSI - (F/G)
    35 IF((ABSF(H - PSI)) - .0001) 37,37,36
    36 PSI = H
       GO TO 32
C24          END OF ITERATION
    37 PSI = H
    27 CD0 = - 0.434294 * LOGF(CD(I)) + 0.5 * W * (ETA(I) - PSI)
    38 X(I) = ETA(I) + PSI
    39 Y(I) = PSI + 0.434294*(LOGF(CD(I)))/W
    21 CD(I) = 1000. * CD(I)
    40 PUNCH 41, N1(I), N2(I), N3(I), ETA(I), CD(I), CAP, PSI, PHI0, CD0,
      1X(I), Y(I)
    50 CONTINUE
C
    51 PUNCH 52, K
C
C26    NOW COMES THE LEAST-SQUARES PART
    53 SX = 0.
       SY = 0.
       SXX = 0.
       SXY = 0.
       SYY = 0.
    54 DO 60 I = 1, K
    55 SX = SX + X(I)
    56 SY = SY + Y(I)
    57 SXX = SXX + X(I)*X(I)
    58 SXY = SXY + X(I)*Y(I)
    59 SYY = SYY + Y(I)*Y(I)
    60 CONTINUE
```

```
   61 FN = K
   62 DN = 1./FN
   63 AVX = SX * DN
   64 AVY = SY * DN
   65 DNN = 1./(FN - 1.)
   66 S = SXX - SX * AVX
   67 COVX = S * DNN
   68 COVY = (SYY - SY * AVY) * DNN
   69 COVXY = (SXY - SX * AVY) * DNN
   70 STDX = SQRTF (COVX)
   71 STDY = SQRTF (COVY)
   72 CORR = COVXY/(STDX * STDY)
   73 A = COVXY/COVX
   74 B = AVY - A*AVX
   75 SR = SQRTF((FN-1.)*(COVY-A*A*COVX)/(FN - 2.))
   76 SI = SR * SQRTF(DN + AVX * AVX / S)
   77 SS = SR * SQRTF (1./S)
   78 PUNCH                  79, CORR, A, B, SR, SS, SI
   80 CDOP = -B * W
   81 CONFA = 1.65 * SS
   82 CONFB = -1.65 * SI * W
   83 PUNCH                  84, A, CONFA, CDOP, CONFB
C27          THUS ENDS THE LEAST SQUARES PART
   85 READ 2, TITLE
   86 IF (TITLE(1) - .455544) 87, 88, 87
   88 TYPE 2, TITLE
   89 PUNCH 2, TITLE
   90 CALL EXIT
   87 GO TO 3
C
    2 FORMAT (20A4)
    6 FORMAT (F8.2, F8.5, 4F8.3)
    8 FORMAT (//8H TEMP = F8.2/8H CONC = F8.5/8H ETAZ = F8.3/8H CAPO =
     1F8.3/8H CAP1 = F8.3/8H CAP2 = F8.3//37H LEAST-SQUARES FOR ALPHA AN
     2D IO-PRIME    )
   12 FORMAT    (77H1 RUN NO.      ETA  CURR DENS     CAP      PSI     PHI  -
     1LOGIOPRIME  X          Y     /62H                VOLTS MA/SQ.CM  MF/SQ.
     2CM  VOLTS  VOLTS (ALPHA=.5) )
   15 FORMAT (F10.8, F8.4, 51X, 3I3, I1)
   41 FORMAT (1X, 3I3, F8.3, F10.4, 3F8.3, 3F9.3)
   52 FORMAT (/12H THERE ARE  I2,24H DATA POINTS IN THIS SET)
   79 FORMAT (//31H CORRELATION BETWEEN X AND Y = F10.5/22H SLOPE OF LIN
     1E Y(X) = F10.5/26H INTERCEPT OF LINE Y(X) = F10.5/31H STANDARD ERR
     2OR OF ESTIMATE =  F10.5/31H CONFIDENCE INTERVAL PARAMETERS/22X,10H
     3 SLOPE    F10.5/22X,10H INTERCEPT F10.5)
   84 FORMAT (/41H CATHODIC TRANSFER COEFFICIENT, ALPHA =  F10.5/32H 95
     1PERCENT CONFIDENCE LIMITS = F8.3//41H CORRECTED EXCHANGE CURRENT,
     2-LOG IO  =  F9.3/32H 95 PERCENT CONFIDENCE LIMITS =  F8.3)
      END
```

FORMS FOR INPUT DATA TO PROGRAM 5

The input to Program 5, the second part of the overvoltage calculations, should consist of the following cards:

CARD 1:

Column 1: A "1" should appear in column 1.

Columns 2-80: This space is for a title.

CARD 2:

Columns 1-8: TEMP, the temperature, ^{o}C. Two decimal places.

Columns 9-16: CONC, the electrolyte concentration, in moles/liter. Five decimal places.

Columns 17-24: ETAZ, the zero charge point of the amalgam with respect to the same reference electrode as the overpotential measurements. Three decimal places.

Columns 25-32: CAPO, K_o in equation (6), $\mu f/cm^2$. Three decimal places.

Columns 33-40: CAP1, K_1 in equation (6), $\mu f\ cm^{-2}\ volt^{-1}$. Three decimal places.

Columns 41-48: CAP2, K_2 in equation (6), $\mu f\ cm^{-2}\ volt^{-2}$. Three decimal places.

This is followed by data cards in the following format:

DATA CARDS:

Columns 1-10: CD (I), current density, amp/cm^2. Eight decimal places.

Columns 11-18: ETA (I), overpotential, volts. Four decimal places.

Columns 70-79: Identification number

Program 4 produces output cards in precisely this format, so that it is necessary only to select the desired cards for input to Program 5.

LAST CARD:

The last card of the data set should be blank.

The last card of the entire deck should read "END" in columns 1-3.

NOTE:

The program has been written with the convention that cathodic overpotentials are taken to be positive. A zero-charge point which is negative with respect to the zero-overpotential point should be given a positive value also. If both the overpotentials and the zero-charge point are given the conventional signs for electrode potentials (negative for cathodic, positive for anodic), the program must be modified as follows:

Statement 28 should read "PHIO = ETA (1) - ETAZ".

A statement should be inserted after statement 37, which reads "ETA (1) = - ETA (1) ".

A statement should be inserted after statement 21, which reads "ETA (1) = - ETA (1)" .

```
1 MERCURY 1-22-64 BOOK 96, PAGE 19, RUNS 1-11
   26.2    .1          .165  26.6     18.65     9.65        96 19    MERCURY
 .10711318  1.2802                                                    96 19   11
 .06614743  1.2555                                                    96 19   11
 .04126667  1.2308                                                    96 19   11
 .03089814  1.2166                                                    96 19   11
 .02365379  1.2027                                                    96 19   11
 .01971218  1.1938                                                    96 19   11
 .08170679  1.2636                                                    96 19   22
 .04558101  1.2325                                                    96 19   22
 .03012561  1.2104                                                    96 19   22
 .01888411  1.1865                                                    96 19   22
 .01380436  1.1718                                                    96 19   22
 .00924673  1.1528                                                    96 19   22
 .00696264  1.1405                                                    96 19   22
 .02097022  1.1915                                                    96 19   33
 .01066125  1.1576                                                    96 19   33
 .00635090  1.1324                                                    96 19   33
 .00385451  1.1084                                                    96 19   33
 .00290654  1.0943                                                    96 19   33
 .00255973  1.0886                                                    96 19   33
 .00476340  1.1191                                                    96 19   44
 .00270185  1.0935                                                    96 19   44
 .00164911  1.0713                                                    96 19   44
 .00220697  1.0839                                                    96 19   65
 .00079137  1.0372                                                    96 19   65
 .00046663  1.0163                                                    96 19   65
 .00036849  1.0062                                                    96 19   65
 .00024047   .9824                                                    96 19   76
 .00014127   .9585                                                    96 19   76
 .00011258   .9491                                                    96 19   76

END   OF RUN    96 19   MERCURY
```

1 MERCURY 1-22-64 BOOK 96, PAGE 19, RUNS 1-11
TEMP = 26.20
CONC = .10000
ETAZ = .165
CAP0 = 26.600
CAP1 = 18.650
CAP2 = 9.650

LEAST-SQUARES FOR ALPHA AND IO-PRIME

1 RUN NO.			ETA VOLTS	CURR DENS MA/SQ.CM	CAP MF/SQ.CM	PSI VOLTS	PHI VOLTS	-LOGIOPRIME (ALPHA=.5)	X	Y
96	19	1	1.280	107.1131	17.802	-.116	-1.115	12.729	1.163	-.174
96	19	1	1.255	66.1474	17.737	-.115	-1.090	12.719	1.139	-.185
96	19	1	1.230	41.2666	17.684	-.114	-1.065	12.704	1.116	-.196
96	19	1	1.216	30.8981	17.659	-.113	-1.051	12.704	1.103	-.203
96	19	1	1.202	23.6537	17.638	-.112	-1.037	12.696	1.090	-.209
96	19	1	1.193	19.7121	17.626	-.112	-1.028	12.696	1.081	-.213
96	19	2	1.263	81.7067	17.757	-.116	-1.098	12.699	1.147	-.180
96	19	2	1.232	45.5810	17.687	-.114	-1.067	12.676	1.118	-.194
96	19	2	1.210	30.1256	17.649	-.113	-1.045	12.660	1.097	-.203
96	19	2	1.186	18.8841	17.618	-.111	-1.021	12.650	1.074	-.214
96	19	2	1.171	13.8043	17.604	-.110	-1.006	12.656	1.060	-.221
96	19	2	1.152	9.2467	17.593	-.109	-.987	12.661	1.042	-.230
96	19	2	1.140	6.9626	17.589	-.109	-.975	12.675	1.031	-.237
96	19	3	1.191	20.9702	17.624	-.112	-1.026	12.649	1.079	-.211
96	19	3	1.157	10.6612	17.595	-.110	-.992	12.642	1.047	-.227
96	19	3	1.132	6.3509	17.589	-.108	-.967	12.643	1.023	-.239
96	19	3	1.108	3.8545	17.594	-.107	-.943	12.647	1.000	-.250
96	19	3	1.094	2.9065	17.602	-.106	-.929	12.644	.987	-.257
96	19	3	1.088	2.5597	17.606	-.106	-.923	12.649	.982	-.260
96	19	4	1.119	4.7634	17.590	-.108	-.954	12.650	1.011	-.246
96	19	4	1.093	2.7018	17.602	-.106	-.928	12.669	.986	-.259
96	19	4	1.071	1.6491	17.623	-.105	-.906	12.686	.965	-.270
96	19	6	1.083	2.2069	17.610	-.106	-.918	12.671	.977	-.263
96	19	6	1.037	.7913	17.674	-.103	-.872	12.702	.933	-.287
96	19	6	1.016	.4666	17.716	-.102	-.851	12.745	.913	-.300
96	19	6	1.006	.3684	17.740	-.101	-.841	12.758	.904	-.305
96	19	7	.982	.2404	17.803	-.100	-.817	12.732	.881	-.315
96	19	7	.958	.1412	17.877	-.099	-.793	12.750	.859	-.327
96	19	7	.949	.1125	17.909	-.098	-.784	12.765	.850	-.333

THERE ARE 29 DATA POINTS IN THIS SET

CORRELATION BETWEEN X AND Y = .99884
SLOPE OF LINE Y(X) = .50967
INTERCEPT OF LINE Y(X) = -.76365
STANDARD ERROR OF ESTIMATE = .00219
CONFIDENCE INTERVAL PARAMETERS
SLOPE .00472
INTERCEPT .00485

CATHODIC TRANSFER COEFFICIENT, ALPHA = .50967
95 PERCENT CONFIDENCE LIMITS = .007

CORRECTED EXCHANGE CURRENT, -LOG IO = 12.854
95 PERCENT CONFIDENCE LIMITS = -.134

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